Synthesis Of Ni Nanoparticle
By W/O Emulsion Combustion Under Fuel Rich Conditions

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Abstract: Emulsion Combustion Method (ECM) is a new method for producing ultrafine particles. In this method, W/O (water-in-oil) emulsion droplets containing a metal salt solution as the precursor of the product were sprayed into a high temperature furnace. The produced particles have advantages that their chemical purity is high and their size distribution is narrow. They were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). Existence of Ni nanoparticle in carbon matrix was confirmed by TEM observation and the diameter was about 10 nm. On the other hand, the calcinated NiO particles were spherical with a range from 0.25 to 1 µm by SEM observation. SEM and TEM observation reveals that particles size distribution has slightly dispersed. Clear peaks due to metal nickel as well as nickel oxide were confirmed. Therefore, it was clarified the synthesized particles by the ECM consisted of metal Ni and NiO.

Keywords: Ni nanoparticle, W/O emulsion, Combustion

1. INTRODUCTION

Recently, demand for various electronic devices has increased against a background of advancement of information society. We focused on Multi Layer Ceramic Capacitor (MLCC) used for electronic equipments because it is one of the most common capacitors. MLCC structure was formed by multi lamination Ni internal electrodes and dielectric substances. Miniaturization and increase of capacity of MLCC have been required. Therefore, the electrodes will be thinned and multilayered as one of the solutions. Then Ni nanoparticle is expected to obtain. Ni particles have been produced by Chemical Vapor Deposition (CVD) but there is an issue that size control of produced particles is difficult. In response, it has been reported that fine nickel oxide particles are reduced by using hydrogen of 5 vol%[1] and nickel powders is synthesized by laser-induced reactions between a nickel nitrate hexahydrate precursor and 2-ethoxyethanol-based mixtures[2]. On the other hand, more effectively and industrially manufacturing process has been required to produce a large amount of ultrafine particles. Then, synthesis of Ni nanoparticle by W/O emulsion combustion method (ECM) was proposed[3-6].

In this method, W/O emulsion including many droplets of a metal salt solution as the precursor of the product are sprayed into high temperature furnace. Subsequently, the fine droplets are dried, decomposed, reduced, and sintered by combustion heat of the oil phase. Produced particle size is determined by droplet size of water solution and the concentration of a metal solution, assuming that one particle is produced by one droplet of water solution. Therefore, their particles size can be controlled by emulsion structure.

The main aim of this work is to obtain ultrafine and monodispersed Ni particles and improve its productivity by the combustion of W/O emulsion under fuel rich condition. Then the effect that emulsion structure and combustion condition had on particles size, shape and composition was investigated.

2. EXPERIMENTAL

2.1 Preparation of W/O emulsion

Ni(NO₃)₂ • 6H₂O (Kanto Chem. Co., Ltd) was dissolved to water. Emulsion was formed by adding this aqueous solution to a mixture of n-dodecane and surfactants (Span 80, Tween 20: TOKYO KASEI KOGYO CO., Ltd), using a magnetic stirrer. Finally, the mixture was stirred by using ultrasonic homogenizer (20 kHz) and the W/O emulsion was prepared. Condition of emulsion preparation is shown in Table 1 and concentration of Ni solution was 1M. Emulsion was prepared with Span 80:Tween 20 (62:38).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass[g]</th>
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<tbody>
<tr>
<td>Ni(NO₃)₂ • 6H₂O</td>
<td>0.58</td>
</tr>
<tr>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>n-dodecane</td>
<td>20</td>
</tr>
<tr>
<td>Span 80</td>
<td>3.27</td>
</tr>
<tr>
<td>Tween 20</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Table 1 Condition of W/O emulsion preparation

2.2 Apparatus and procedure

Figure 1 shows a schematic diagram of experimental apparatus. The apparatus consists of an atomizer for W/O emulsion, a reactor and a particle collection device. A liquid phase pump supplied the W/O emulsion to the spray nozzle at a feed rate of 1.76 g/min, where it was atomized upward by 4 l/min of methane. Air of 45 l/min as oxidant gas was provided through two holes that were placed at the sidewall of the reactor with 40 mm in inner diameter. The reactor is surrounded by an electric heater.

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Moreover, the temperature of the heater was set to 973K to avoid heat loss. The obtained particles were observed by scanning electron microscopy (SEM) and transmission (TEM), and identified by X-ray diffraction (XRD).

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric analysis

Thermogravimetric analysis for Ni(NO$_3$)$_2$•6H$_2$O was carried out to investigate the property of thermal decomposition. Figure 2 shows these results. Here, analysis was carried out under air, oxygen, hydrogen or nitrogen atmosphere with a heating rate of 1 K/s.

Thermal decomposition progressed through three stages in any condition. The first two steps corresponded to elimination reaction of crystal water and the third step to decomposition of metal salt. NiO was produced under inert or oxidative atmosphere but metal Ni was produced under reducing atmosphere over 600 K. Thus reducing gas such as hydrogen is essential to produce metal Ni. Based on these results, combustion conditions were determined.

3.2 Stability of W/O emulsion

Stability of W/O emulsion was investigated as a measure of hydrophilic-lipophilic balance (HLB). The HLB is one of the ways of predicting emulsion type. Assuming one surfactant has no interaction with another surfactant, the HLB has additive property. Therefore, the HLB of a mixture of two surfactants can be determined.

The HLB was changed from 5 to 13. In low HLB(5-7) and high HLB(11-13), the phase separation was observed and droplet size of water phase was large. In the HLB 8-10 region, the phase separation did not occur and the droplet size of water phase was small. According to these results, optimum surfactant ratio (Span 80 : Tween 20 = 62:38) was determined.

3.3 Analysis of produced particles

Collected particles contained carbon and it is difficult to confirm Ni or NiO particles with eyes. Figure 3 shows SEM photograph of produced particles by W/O emulsion combustion. Here, they were incinerated at 800 K to eliminate carbon before SEM observation. So these particles were considered NiO. They were spherical and the range of their size was from 0.25 to 1 µm.

On the other hand, existence of Ni or NiO particles in carbon matrix was confirmed from TEM observation. The photograph is shown in Fig. 4. There are Ni particles in circled areas on the photo and the diameter was about 10 nm.

Ni nanoparticle were produced by W/O emulsion combustion. However, these two photographs reveals
that particles size distribution has dispersed. The tendency can be attributed to coalescence of water phase or unstability of combustion. It is considered ultrafine particles on TEM photo were produced from dispersed fine water phase and particles on SEM photo were produced from aggregated coarse water phase.

XRD analysis was carried out to identify the produced particles. The result is shown in Fig. 5. Clear peaks due to metal Ni as well as NiO were confirmed. Therefore, the mixture of Ni and NiO nanoparticles could be produced by W/O emulsion combustion under fuel rich condition. The result is attributable to reducing gas such as hydrogen and carbon monoxide generated by water gas reaction.

4. CONCLUSIONS
W/O emulsion combustion for production Ni nanoparticle was carried out and the effect that emulsion structure and combustion condition had on particles size, shape and composition was investigated. It was found that

i) From SEM observation, the produced particles were spherical with range from 0.25 to 1 \( \mu \)m.

ii) Existence of Ni nanoparticle was confirmed by TEM observation and the diameter was about 10 nm.

iii) Complex of metal Ni and NiO was synthesized under fuel rich combustion from XRD analysis.

Particles size distribution has slightly dispersed. It is important to keep stable emulsion, which consisted of fine droplets of water phase, in order to obtain narrow size distribution.

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REFERENCES
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2. Dobbins et al., 1999